PB90-116583

Application of Low NOx Precombustor Technology to the Incineration of Nitrogenated Wastes

Acurex Corp., Research Triangle Park, NC

Prepared for:

Environmental Protection Agency, Research Triangle Park, NC

1989

U.S. Department of Commerce
National Technical Information Service
NTIS

AEERL-P-506

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO. EPA/600/D-89/181	2.	3. PB90-116583
4. TITLE AND SUBTITLE Application of Low NOx Precombustor Technology to the Incineration of Nitrogenated Wastes		5. REPORT DATE 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. Srivastava, J. Ryan (Acurex); W. Linak, R. Hall, J. McSorley (EPA/AEERL); J. Mulholland (MIT)*		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation 4915 Prospectus Drive Durham, North Carolina 27713		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-02-3988 and 68-02-4701
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Published paper; 2/89 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is William P. Linak, Mail Drop 65, 919/541-5792. Presented at AWMA annual meeting, Anaheim, CA, 6/25-30/89.(*)Massachusetts Institute of Technology, Cambridge, MA 02139.

16. ABSTRACT The paper gives results of an evaluation of a 0.6 MW precombustion chamber burner/package boiler simulator, designed for in-furnace NOx control and high combustion efficiency, for high nitrogen content fuel combustion/waste incineration application. The 250-750 ms residence time precombustion chamber burner, using air staging and in-furnace natural gas reburning, yields up to four stoichiometric zones. During initial evaluation, natural gas, doped with NH3 to yield a 5.8% fuel nitrogen content, and No. 2 fuel oil, doped with pyridine to yield a 2.0% fuel nitrogen content, were used to simulate high nitrogen content fuel/waste mixtures. Minimum NO emission levels of 160 and 110 ppm (corrected to 0% O2) were achieved for the natural gas and fuel oil tests, respectively. These results correspond to about 85% reduction in NOx emissions compared to uncontrolled emissions from a conventional burner mounted on a 0.7 MW commercial package boiler. CO emissions for both low NOx tests were < 35 ppm, indicating combustion efficiencies (CEs) > 99%. Pyridine destruction efficiency (DE) was >99.99%. Subsequently, an examination of the incineration characteristics of a nitrogenated pesticide, containing dinoseb in an organic solvent, was conducted on the low NOx facility. NO emissions without in-furnace controls were reduced from 4400 to < 150 ppm with controls.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Nitrogen Oxides	Stationary Sources	07B
Incinerators	Nitrogenated Wastes	
Waste Disposal	Precombustion	15E
Combustion		21B

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 23 22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

EPA/600/D-89/181

APPLICATION OF LOW NO_x PRECOMBUSTOR TECHNOLOGY TO THE INCINERATION OF NITROGENATED WASTES

R.K. Srivastava, J.V. Ryan
Acurex Corporation
4915 Prospectus Dr.
Durham, NC 27713

W.P. Linak, R.E. Hall, J.A. McSorley
Combustion Research Branch, MD-65
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

J.A. Mulholland
Department of Chemical Engineering, 66-419
Massachusetts Institute of Technology
Cambridge, MA 02139

ABSTRACT

A 0.6 MW (2,000,000 Btu/hr) precombustion chamber burner/package boiler simulator facility, designed for in-furnace nitrogen oxide (NO_x) control and high combustion efficiency, has been evaluated for high nitrogen content fuel combustion/waste incineration application. The 250 to 750 ms residence time precombustion chamber burner, using air staging and in-furnace natural gas reburning, yields up to four stoichiometric zones.

During initial facility evaluation, natural gas, doped with ammonia (NH_3) to yield a 5.8 percent fuel nitrogen content, and No. 2 distillate fuel oil, doped with pyridine (C_5H_5N) to yield a 2.0 percent fuel nitrogen content, were used to simulate high nitrogen content fuel/waste mixtures. Minimum nitric oxide (NO) emission levels of 160 and 110 ppm (corrected to 0 percent oxygen, O_2) were achieved for the natural gas and fuel oil tests, respectively. These results correspond to approximately 85 percent reduction in NO_x emissions compared to uncontrolled emissions from a conventional burner mounted on a 0.7 MW (2,500,000 Btu/hr) commercial package boiler. Carbon monoxide (CO) emissions for both low NO_x tests were less than 35 ppm, indicating combustion efficiencies (CEs) greater than 99 percent. Pyridine destruction efficiency (DE) was greater than 99.99 percent.

Subsequently, an investigation examining the incineration characteristics of a nitrogenated pesticide, containing dinoseb (2-sec-butyl-4,6 dinitrophenol) in an organic solvent, was

conducted on the low NO_x facility. The dinoseb formulation contained 6.4 percent nitrogen. NO emissions without any in-furnace NO_x control strategy exceeded 4400 ppm (0 percent O_2). When NO_x controls, in the form of air staging and natural gas reburning, were employed, these emissions were reduced to below 150 ppm. CO emissions were always less than 25 ppm. Dinoseb DE was greater than 99.99 percent and particulate emissions were less than the RCRA limit of 180 mg/dsm^3. Several common products of incomplete combustion (PICs) were identified in the exhaust gases at concentrations typically less than 10 ppb.

INTRODUCTION

Oxides of nitrogen (NO_x) are formed during combustion by the oxidation of atmospheric nitrogen (N_2) and nitrogen contained in the fuel. Nitrogen dioxide (NO_2) is a toxic gas that the U.S. Environmental Protection Agency (EPA) has designated as a criteria pollutant because of its adverse effects on human health.(1) NO_x emitted from stationary combustion sources contribute to the degradation of air quality as well as to acid deposition and forest damage.(2) Increasing levels of atmospheric nitrous oxide (N_2O) have also been measured. Although the sources of this increase have not been determined, these increasing levels have been predicted to contribute to both a decline in stratospheric ozone concentrations and an increase in global climate warming.(3)

Unlike sulfur oxide (SO_x) emissions, NO_x emissions have been increasing in recent years.(4) While coal- and oil-fired utility and industrial boilers account for over half of these NO_x emissions, only 15 percent of these stationary sources are regulated by EPA's New Source Performance Standards (NSPS).(5) The remaining sources must be addressed with retrofit technologies if significant NO_x emission reduction is to be realized. Another NO_x control problem is posed by the incineration of high nitrogen content wastes in hazardous waste incinerators and industrial boilers. While incineration of these materials may not constitute a significant increase in the overall national NO_x emission levels, individual plant emissions may be sufficient to result in a local NO_x problem thus preventing on-site thermal destruction from being permitted. With thermal destruction becoming an increasingly attractive alternative to landfill storage of wastes, there continues to be a need for developing high efficiency, low NO_x combustion technologies. Additionally, incinerator operating conditions which maximize waste destruction are typically those that promote the formation of NO_x.

NO_x species are formed in practical combustion systems by high temperature thermal fixation of atmospheric nitrogen (N_2, source of thermal NO_x)(6) and by oxidation of nitrogen chemically bound in the fuel (source of fuel NO_x).(7) Thermal NO_x can be reduced by decreasing peak flame temperatures. Fuel NO_x, not as strongly dependent on temperature, is very sensitive to reactant stoichiometry. Fuel-rich conditions promote N_2 formation over nitric oxide (NO) formation. Thus, many of the NO_x control technologies currently in use involve modifications of the combustion process to reduce peak flame temperatures and create fuel-rich conditions by reducing fuel and oxidizer mixing rates. These modifications, however, frequently result in reduced combustion efficiency (CE) and increased vessel wall corrosion and ash deposition. Furthermore, practical constraints, such as burner and boiler sizes, limit the effectiveness of NO_x control by combustion modification.

In-furnace NO_x control technologies currently in use, including reduced air preheat, load reduction, low excess air, flue gas recirculation, overfire air, deep air staging, fuel staging (or reburning), and various low-NO_x burner systems, can reduce NO_x emissions by 20 to 80 percent. While these technologies are sufficient to meet current NSPS requirements, new technologies will be required if more stringent NO_x emissions regulations are enacted. EPA has been involved in the development of two evolving NO_x control technologies: the precombustion chamber burner and reburning. These two combustion modification strategies provide alternatives to expensive post-combustion NO_x control technologies, such as selective catalytic reduction which is being utilized extensively in Japan and West Germany. The goal of this experimental program was to utilize the precombustion chamber burner and reburning concepts in developing a low-NO_x, high efficiency combustion system that is practical for both new and retrofit applications.

BACKGROUND

Precombustion Chamber Burner

The precombustion chamber burner is a staged combustion technology capable of achieving NO_x emissions of less than 0.1 lb (as NO_2)/10^6 Btu (or approximately 90 ppm NO_x), even with high nitrogen content fuels.(8) The burner, described by Englund et al.,(8) consists of a primary air and fuel injection system, a large refractory lined precombustion chamber, and a secondary staged air injection section. Fuel and primary air are injected so as to promote rapid mixing in the nearly adiabatic precombustion chamber with a first stage stoichiometry of between 0.6 and 0.8. Residence times between 0.6 and 1.0 sec allow for maximum reduction and conversion of fuel nitrogen species to N_2 in the fuel-rich precombustion chamber. First-stage combustion gases exit the burner through a convergent transition section which minimizes both radiative heat loss to the boiler and back-mixing of the secondary air. The transition section between the burner and boiler is water-cooled to reduce combustion gas temperatures before further air addition and thus minimize the formation of thermal NO_x.

The precombustion chamber burner has been tested on a full-scale (16 MWt) crude-oil-fired steam generator used for thermally enhanced oil recovery (TEOR).(9) A 30-day continuous monitoring test using heavy residual oil demonstrated the burner's ability to maintain a nominal NO_x emission of 70 ppm and high combustion efficiency. During burner optimization testing, NO_x, carbon monoxide (CO), and smoke emissions were measured over a range of first-stage stoichiometries. These data indicate the sensitivity of NO_x emission to first-stage stoichiometry and the good hydrocarbon burnout characteristics of the burner.

A test designed to demonstrate the potential for using this burner for nitrogenated waste incineration was performed at EPA's Air and Energy Engineering Research Laboratory (AEERL). A pilot- scale (0.6 MWt) precombustion chamber burner was used to incinerate a surrogate nitrogenated waste mixture of 9.1 percent (by volume) pyridine (C_5H_5N) in No. 2 distillate fuel oil. NO_x emissions of less than 100 ppm were maintained, with greater than six nines (99.9999%) destruction of pyridine being achieved. The relative NO_x emissions, with and without pyridine addition, indicate that less than 1 percent of the fuel nitrogen

was converted to NO. This preliminary result sparked interest in utilizing the precombustion chamber burner for low NO_x, high efficiency incineration.

While the precombustion chamber burner has been demonstrated successfully in pilot and full-scale tests, its large size and heavy refractory composition make it impractical for most boiler retrofit applications. Reducing the burner size results in insufficient first-stage residence time to fully convert fuel nitrogen to N_2. However, further NO_x control can be achieved by further fuel and air staging (reburning) in the boiler. Current research is investigating the use of light weight refractories to provide improved response to load changes.

Reburning

Reburning is an in-furnace NO_x control technology in which portions of the fuel and combustion air streams are diverted downstream of the primary flame. In this way, the combustor has three distinct zones: a fuel-lean primary zone, a fuel-rich reburning zone, and a fuel-lean burnout zone. NO_x reduction via reburning occurs both by combustion of a portion of the fuel under fuel-rich stoichiometries (conditions not promoting NO_x formation), and chemical destruction mechanisms involving secondary flame radical reactions with NO, resulting in N_2 formation. An EPA study (10) has shown that 50 percent NO_x reduction is possible with 15 to 20 percent of the fuel used for reburning. At low primary NO_x levels, however, a nitrogen-free reburning fuel (such as natural gas) must be used to achieve 50 percent reduction. Reburning can be used in conjunction with other NO_x control schemes to yield lower NO_x emissions. However, application of reburning often necessitates hardware modifications to the combustor.

LOW NO_x EXPERIMENTAL FACILITY

The pilot-scale experimental facility, shown schematically in Figure 1, consists of a vertical precombustion chamber low-NO_x burner and a horizontal package boiler simulator. The precombustion chamber consists of a primary fuel and air injection module, several 0.25 m long spool modules with 0.51 m inside diameter (I.D.), and a convergent elbow module. The modular design of the precombustor permits variation in nominal first-stage residence time between 250 and 750 ms. The modules have a thick refractory wall lining to minimize heat loss and, thus, maintain high temperatures that promote conversion of fuel nitrogen to N_2 under fuel-rich stoichiometries. To achieve rapid mixing in the precombustion chamber, the primary fuel is injected through a divergent nozzle, and the primary air, which is not preheated, is passed through fixed swirl vanes. The convergent elbow module minimizes back-mixing of combustion gas and radiation losses to the boiler. A water-cooled transition module, 0.25 m I.D., cools the combustion gas before secondary air addition to minimize thermal NO_x generation.

The pilot-scale boiler simulator is rated at 0.9 MW thermal input. The boiler's radiant section is horizontal, 0.6 m I.D., 3.0 m long, and cooled with Dowtherm G heat transfer fluid. Combustion gas exits the boiler through a vertical stack. The burner/boiler transition section allows for radial addition of staged air. Additionally, the boiler's front face has two ports for addition of staged (reburn) fuel at an angle of 45 degrees off axis and six axial ports for the addition of burnout air. This design allows for reburning application

from the boiler front face, with aerodynamic separation of the fuel-lean, fuel-rich, and fuel-lean zones in the boiler.

The experimental facility is designed for independent control and measurement of each fuel, fuel dopant (if any), and air stream. Stack gas species are measured by continuous emissions monitors (CEMs). These monitors include measurement of NO, NO_x, O_2, CO, CO_2, and total unburned hydrocarbons (THC). All data are reported corrected to 0 percent O_2 dry basis.

BURNER PERFORMANCE EVALUATION

Natural gas, doped with ammonia (NH_3) to yield a 5.8 percent fuel nitrogen content, and No. 2 distillate fuel oil, doped with pyridine (C_5H_5N) to yield a 2 percent fuel nitrogen content, were used to simulate high nitrogen content fuel/waste mixtures. In these tests, the shortest burner configuration, corresponding to a first-stage nominal residence time of 250 ms, was evaluated. A 0.7 MW North American fire-tube package boiler was used to provide conventional burner results for comparison with the multistaged burner results. This boiler is a three-pass unit with a continuous service rating of 0.3 kg of steam per second (2400 lb/hr). Its size and thermal characteristics are similar to those of the package boiler simulator.(11)

Burner baseline performance (air staging) and burner operation with reburning (fuel staging) were evaluated. The parameters affecting the NO_x emissions from the facility without reburning are fuel nitrogen content, combustion gas residence time in the prechamber, first-stage stoichiometry, and exhaust stoichiometry. The residence time of combustion gas in the burner depends on precombustion chamber length, load, and stoichiometry. The nominal load was 0.6 MW. The exhaust stoichiometry was kept at a nominal value of 15 percent excess air. First-stage stoichiometry was optimized for each parametric test sequence. The experimental matrix describing the tests conducted is shown in Table 2.

Burner Stoichiometry Variation

First-stage stoichiometry was varied by changing the primary air flow. Secondary radial air was adjusted to maintain 15 percent excess air. The results are plotted in Figure 2. The curves indicate a strong sensitivity of stack NO to changes in burner stoichiometry. For the NH_3/natural gas tests, a minimum NO emission of 315 ppm occurred at a burner stoichiometry of about 0.78. For the C_5H_5N/fuel oil tests, a minimum of 190 ppm occurred at a burner stoichiometry of 0.65. By comparison, similar tests using the North American boiler produced NO emissions of 1000 ppm when firing the 5.8 percent nitrogen NH_3/natural gas fuel at 15 percent excess air. NO emissions of 765 ppm resulted when firing the 2 percent nitrogen C_5H_5N/fuel oil mixture at 15 percent excess air. Thus, the low NO_x burner reduced NO emissions by 68 percent for the NH_3/natural gas fuel and by 75 percent for the C_5H_5N/fuel oil mixture.

Excess Air Variation

The effect of excess air variation on stack NO is shown in Figure 3. As expected, excess air had a much stronger effect in the conventional North American boiler tests than in the low NO_x burner tests. While reducing excess air did provide some NO reduction with the low NO_x burner, maintaining an exhaust excess air level of 15 percent is important for achieving high combustion efficiency.

Load Variation

The effect of load reduction on stack NO is shown in Figure 4. As load was decreased from a nominal condition of 0.6 MW to 65 percent of nominal, the stack NO concentration dropped by 20 to 25 percent in the low NO_x burner tests. With a conventional burner, NO emissions are reduced only slightly with burner derating, due to decreased air/fuel mixing intensity. However, with the low NO_x burner, the effect is much greater because load reduction corresponds to an increase in first-stage residence time and, thus, a decrease in NO emission. Reducing load by 35 percent increased burner residence time from 250 to 385 ms.

Fuel Nitrogen Variation

In addition to the base case tests, fuel nitrogen content was varied between 0 and 5.8 percent and 0 and 5.0 percent for the NH_3/natural gas and C_5H_5N/fuel oil tests, respectively. The effect of fuel nitrogen variation is shown in Figure 5. As expected exhaust NO levels increase with increasing fuel nitrogen content. Results from the conventional North American boiler were much more sensitive to this effect. These results demonstrate the precombustion chamber burner's ability to reduce fuel nitrogen to N_2 even at reduced size (250 ms). The full size (600 to 800 ms) precombustion chamber burner produces NO emissions even less sensitive to fuel nitrogen content.(8)

Reburning Tests

For these tests, total boiler load (0.6 MW, 2,000,000 Btu/hr) was held constant while 35 percent of the fuel was diverted from the primary fuel injector to two secondary injectors. The reburn fuel (undoped natural gas) was added through two ports in the boiler front face at an angle of 45 degrees off axis, using water-cooled injectors (see Figure 1). Staged air to complete primary fuel combustion was added radially into the transition section. Burnout air for the reburn fuel was added axially near the boiler wall through six axial ports on the boiler front face. Thus, a four-stage combustion process was established, consisting of a fuel-rich burner zone and three boiler zones characteristic of reburning (i.e, fuel-lean, fuel-rich, fuel-lean). The stoichiometry in the third stoichiometric zone (SR3, the fuel-rich reburning zone in the boiler) is critical in this NO_x control process.

The C_5H_5N/fuel oil and NH_3/natural gas results are given in Figure 6. NO emissions decrease due to both primary NO destruction and primary combustion gas dilution. Two second-stage stoichiometries (SR2) were established (1.1 and 1.0), with 35 percent fuel staging (reburning). The exhaust NO levels were reduced to 120 ppm (from 190 ppm) at a

SR2 of 1.1 (and a SR3 of 0.76) and to 110 ppm at a SR2 of 1.0 (and a SR3 of 0.69) for the C_5H_5N/fuel oil tests. Similarly, NO emissions were reduced to 195 ppm (from 315 ppm) at a SR2 of 1.1 and 160 ppm at a SR2 of 1.0 for the NH_3/natural gas tests. Note that dilution accounts for most of the decreases measured. Due to less distinct stoichiometric zones than typically established in reburning applications, the NO reduction by fuel staging was not quite as great as that obtainable when the staged fuel is injected farther downstream of the fuel-lean second-stage zone.(11) However, the configuration used in these tests requires no additional boiler penetrations other than modifications to the boiler front face. In addition, complete destruction of the primary fuel/waste stream appears to be ensured by providing all of the required primary combustion air prior to entry into the boiler.

Burner performance evaluation results indicate that relatively low NO_x emission levels are possible with a shortened precombustion chamber burner provided the first-stage stoichiometry is optimized and a post-flame NO_x control technology like reburning is used. CO emissions, for all the tests performed during burner performance evaluation, were less than 35 ppm, indicating that combustion efficiencies attained were greater than 99 percent.

NITROGENATED WASTE INCINERATION

Subsequent to the burner evaluation tests, an investigation to examine the incineration characteristics of a nitrogenated pesticide, containing dinoseb (2-sec-butyl-4,6 dinitrophenol), in an organic solvent, was conducted on the low NO_x burner facility. The burner was configured with all its modular sections in place so as to maximize the first stage residence time (750 ms). This dinoseb pesticide product formulation contained 6.4 percent nitrogen. An ultimate analysis and analysis from the material data safety sheet are shown in Table 1. Incineration conditions with no NO_x control, with air staging, and with air staging and reburning were evaluated using the low NO_x burner/package boiler simulator. The North American boiler was not used for these tests. Natural gas was used as the reburn fuel and was added in addition to a fixed primary load of 0.6 MW (2,000,000 Btu/hr). This increase in total load (approximately 32%) differs from the procedure used during the burner evaluation tests where total load was held constant.

A Source Assessment and Sampling System (SASS) train in conjunction with GC/MS analysis was used to characterize emissions of dinoseb and semi-volatile organic products of incomplete combustion (PICs). A Volatile Organic Sampling Train (VOST) in conjunction with GC/MS analysis was used to characterize emissions of volatile PICs. Dinoseb recovery was characterized by spiking 100 g XAD-2 resin with standard dinoseb solutions in dichloromethane. All XAD-2 and particulate filter samples were Soxlet extracted in dichloromethane and methanol, concentrated by Kederna-Danish evaporation, and analyzed by GC/MS. Prior to the incineration tests, scoping tests were carried out to determine the maximum dinoseb product concentration in No. 2 distillate fuel oil for stable operation. During these tests, successively increasing concentrations of dinoseb product in fuel oil were incinerated until combustion conditions deteriorated. However, the scoping tests revealed that 100 percent dinoseb product could be stably combusted. Thereafter, the remaining incineration tests were carried out with 100 percent dinoseb product. The experimental matrix describing the tests conducted is shown in Table 2.

Gaseous and Particulate Emissions

Table 3 presents the stoichiometric and reburning parameters and the gaseous and particulate emissions for the dinoseb product incineration tests. All concentrations are presented dry and corrected to 0 percent O_2. Concentrations corrected to 7 percent O_2 (RCRA convention) are presented in parentheses. Test 7 indicates that NO emissions without any combustion modification for NO_x control exceeded 4400 ppm. When NO_x controls in the form of air staging with and without natural gas reburning were applied, these NO emissions were reduced to below 150 ppm. Thus the use of the precombustor concept reduced the NO emissions by approximately 96 percent. It is interesting to note that reburning did not offer any further NO_x reduction over incineration conditions with air staging only. This is likely because the configuration of the experimental facility provided ample first stage residence time for the conversion of fuel nitrogen to N_2 and further allowed secondary air addition at relatively cool temperatures, thus inhibiting the formation of thermal NO. These effects probably provided a low concentration NO pool before the addition of reburning fuel and so inhibited reburning efficiency.(10) It is interesting to note that the NO_x measurements are very similar to those for NO. In fact, the differences are well within instrument error. This addresses our concern that, because of the nitrogenated nature of dinoseb, NO_2 may be preferentially emitted. We see, however, that, consistent with other nitrogen containing fuels tested, NO_2 is typically less than 5 percent of the total NO_x emitted. It is also important to note that corresponding NO emissions from uncontrolled dinoseb product combustion in industrial boilers would likely be somewhat less than that measured in test 7. The high temperature, adiabatic design of the precombustor promotes thermal NO_x formation when operated fuel-lean. This type of operation, however, is comparable to that used in most hazardous waste incinerators (high temperatures, adiabatic, high excess air, high residence times) and so is of practical interest.

The particulate emissions for all tests were below the RCRA limit of 180 mg/dsm^3, and were determined to consist primarily of calcium sulfate and calcium oxide (particulate analyzed by x-ray diffraction). The particulate emission level for dinoseb product incineration with reburning was less than that for dinoseb product incineration without reburning. This may be partially due to increased secondary flame burnout, but is also due to simple dilution by the addition of natural gas reburn fuel and oxidizer. The CO and unburned hydrocarbon (THC) emissions were less than 15 ppm and 5 ppm, respectively, indicating that the combustion efficiencies were in excess of 99 percent.

Dinoseb Destruction Efficiencies and Products of Incomplete Combustion

No dinoseb was detected in any of the concentrated dichloromethane extract combustion emission samples. These combined XAD-2 and particulate filter extracts were analyzed by GC/MS. These results and the results of dinoseb recovery tests are shown in Table 4. These data indicate that, although the extraction method used resulted in low dinoseb recovery (9.39%), destruction efficiencies (DEs) calculated using measured instrument detection limits could be determined to be greater than the 99.99 percent RCRA limit. Low dinoseb recoveries, however, are not unique to these tests. Efforts by Acurex Corporation on samples from another dinoseb campaign [sponsored by the EPA Risk Reduction

Engineering Laboratory (RREL)] and Battelle Columbus Division performing nitrogenated PIC analyses [for the EPA Health Effects Research Laboratory (HERL)] found similar results.

Qualitative PIC emissions, measured by SASS and VOST sampling in conjunction with GC/MS analysis, are shown in Table 5. Results indicate that several common combustion PICs are present and emitted in concentrations typically less than 10 ppb. It is important to note that these analyses include only qualitative identification of volatile and semi-volatile compounds. These categories approximately correspond to compounds with boiling points below 100 °C and those between 100 to 300 °C, respectively. No information is currently available regarding the potential presence of higher molecular weight compounds including polycyclic aromatic hydrocarbons (PAHs) and nitrogenated PAHs.

CONCLUSIONS

Results from the burner evaluation experimental program indicate that a precombustion chamber burner, shortened in length and coupled with reburning, is most effective in minimizing NO_x emissions and is capable of providing an overall NO reduction of approximately 85 percent. These observations were confirmed in the dinoseb tests, where NO_x reductions of approximately 96 percent were obtained.

The reburning hardware modifications used in this study were designed with retrofit feasibility and efficient combustion in mind. In the reburning tests performed during the evaluation phase, staged fuel and air from the front face of the boiler provided a secondary flame for increased primary fuel/waste destruction.

Finally, the results of this program indicate that the precombustion chamber burner technology is capable of incinerating highly nitrogenated wastes with DEs in excess of 99.99 percent, maintaining low NO_x and PIC emissions, and producing combustion efficiencies in excess of 99 percent. This technology may, therefore, be an attractive alternative for the disposal/destruction of highly nitrogenated wastes.

ACKNOWLEDGMENTS

Portions of this work were conducted under EPA contracts 68-02-3988 and 68-02-4701 with Acurex Corporation. The authors would like to thank C. Pendergraph (Acurex Corp.) and R.A. Grote (EPA/AEERL) for their help operating the combustion and sampling equipment, and to J. Lewtas, D.M. DeMarini, R.R. Watts, and L.D. Claxton (EPA/HERL) for their help with portions of the sample preparation and organic analyses. Additionally, the authors would like to thank D.A. Oberacker (EPA/RREL) for his helpful advice and the U.S. EPA Office of Pesticides and Toxic Substances (OPTS) for partial project funding.

DISCLAIMER

The research described in this paper has been reviewed by the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and

policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

1. Clean Air Act, U.S. Environmental Protection agency, Amended in 1977.

2. Keinhorst, H., "Legal Instruments and the State of Technology for Reducing NO_x Emissions in the Federal Republic of Germany," In: Proceedings: 1985 Symposium on Stationary Combustion NO_x Control, Volume 1: Utility Boiler Applications, EPA-600/9-86-021a (NTIS PB86-225042), July 1986, p. 4-1.

3. Kramlich, J.C., et al., "EPA/NOAA/NASA/USDA N_2O Workshop, Volume I," EPA-600/8-88-079 (NTIS PB88-214911), May 1988.

4. Gerber, C.R., Opening Remarks, In: Proceedings: 1985 Symposium on Stationary Combustion NO_x Control, Volume 1, EPA-600/9-86-021a (NTIS PB86-225042), July 1986, p. 2-1.

5. "Standards of Performance for New Stationary Sources - Volume 1: Summary and Standards," EPA-340/1-82-005a, June 1982.

6. Zeldovich, Y.B.: Acta Physicochimica U.R.S.S. 21, 577 (1946).

7. Pershing, D.W. and Wendt, J.O.L., Sixteenth Symposium (International) on Combustion, p. 389, The Combustion Institute, 1977.

8. England, G.C., et al., "Evaluation and Demonstration of Low- NO_x Burner Systems for TEOR Steam Generators - Design Phase Report," EPA-600/7-84-076 (NTIS PB84-224393), July 1984.

9. England, G.C., et al., "Evaluation and Demonstration of Low- NO_x Burner Systems for TEOR Steam Generators: Final Report - Field Evaluation of Commercial Prototype Burner," EPA-600/7-85-013 (NTIS PB85-185874), March 1985.

10. Mulholland, J.A., et al., "Reburning Application To Firetube Package Boilers," EPA-600/7-87-011 (NTIS PB87-177515), March 1987.

11. Mulholland, J.A., and Hall, R.E., "Fuel Oil Reburning Application for NO_x Control to Firetube Package Boilers," Journal of Engineering for Gas Turbines and Power, Vol. 109, ASME, April 1987, pp. 207-214.

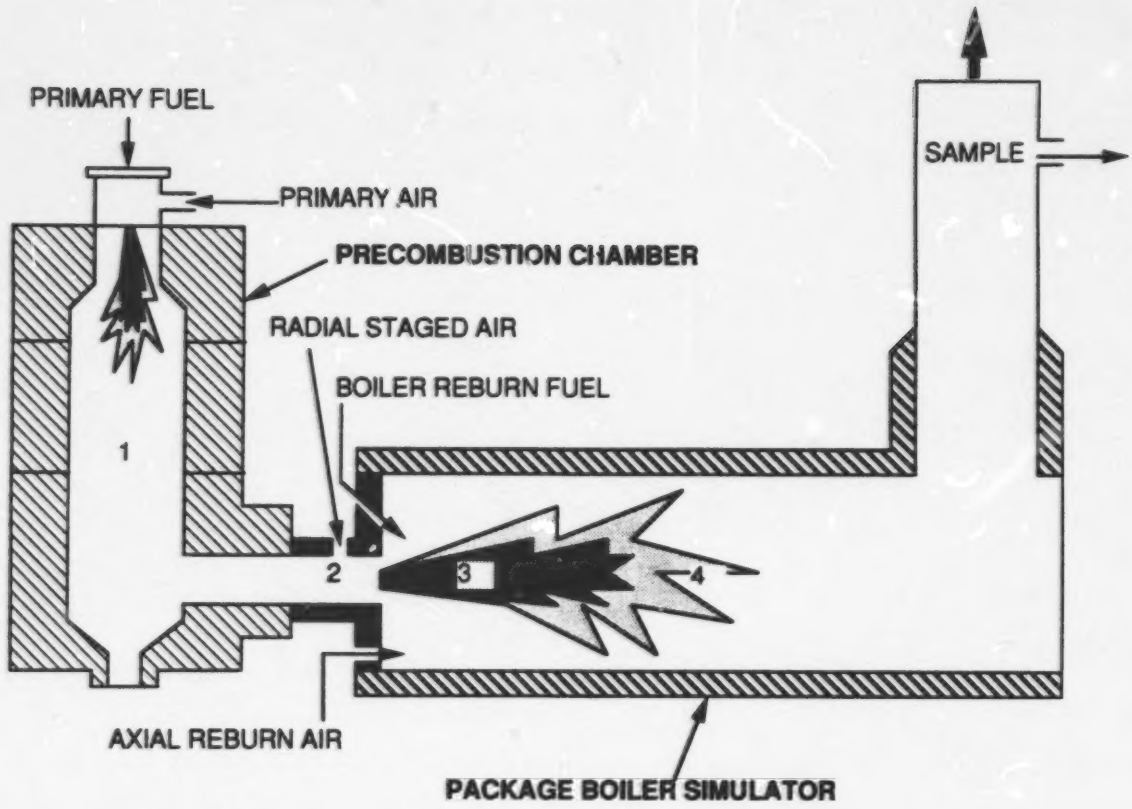

Figure 1. EPA pilot-scale combustion research facility consisting of a refractory-lined precombustion chamber and package boiler simulator, with modified air and fuel staging ports.

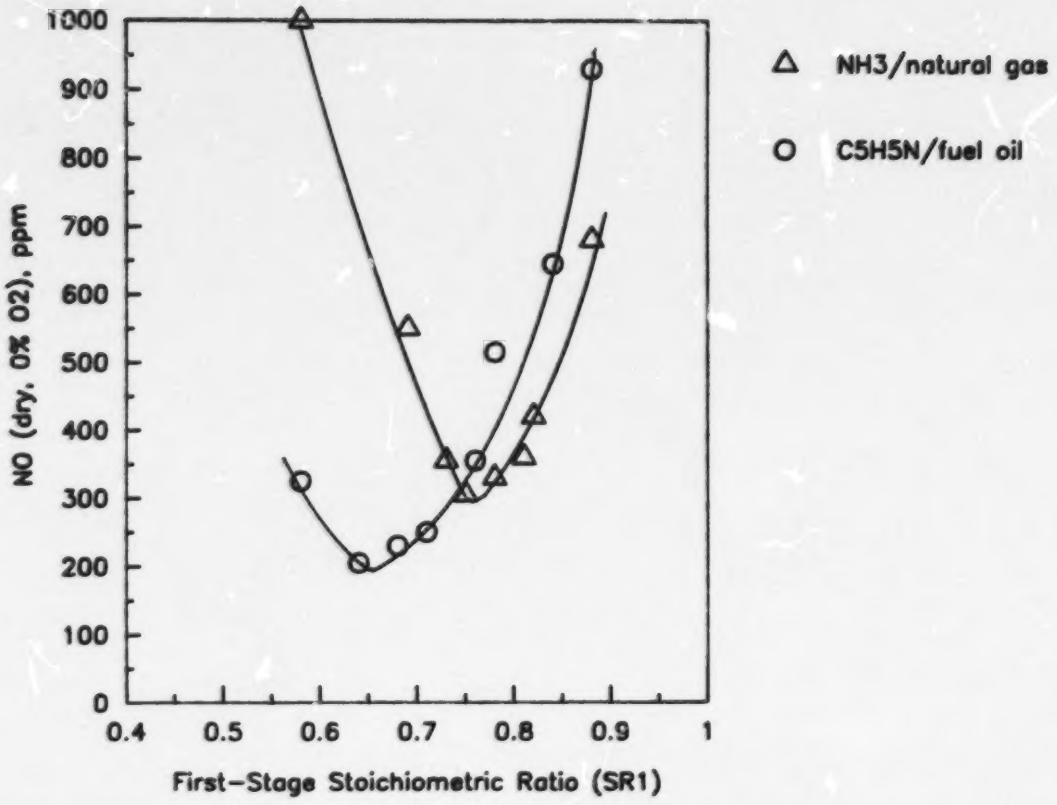

Figure 2. Effect of burner stoichiometry on exhaust NO concentration from tests burning a 5.8 percent fuel nitrogen NH_3/natural gas and a 2 percent fuel nitrogen C_5H_5N/No. 2 distillate fuel oil mixtures.

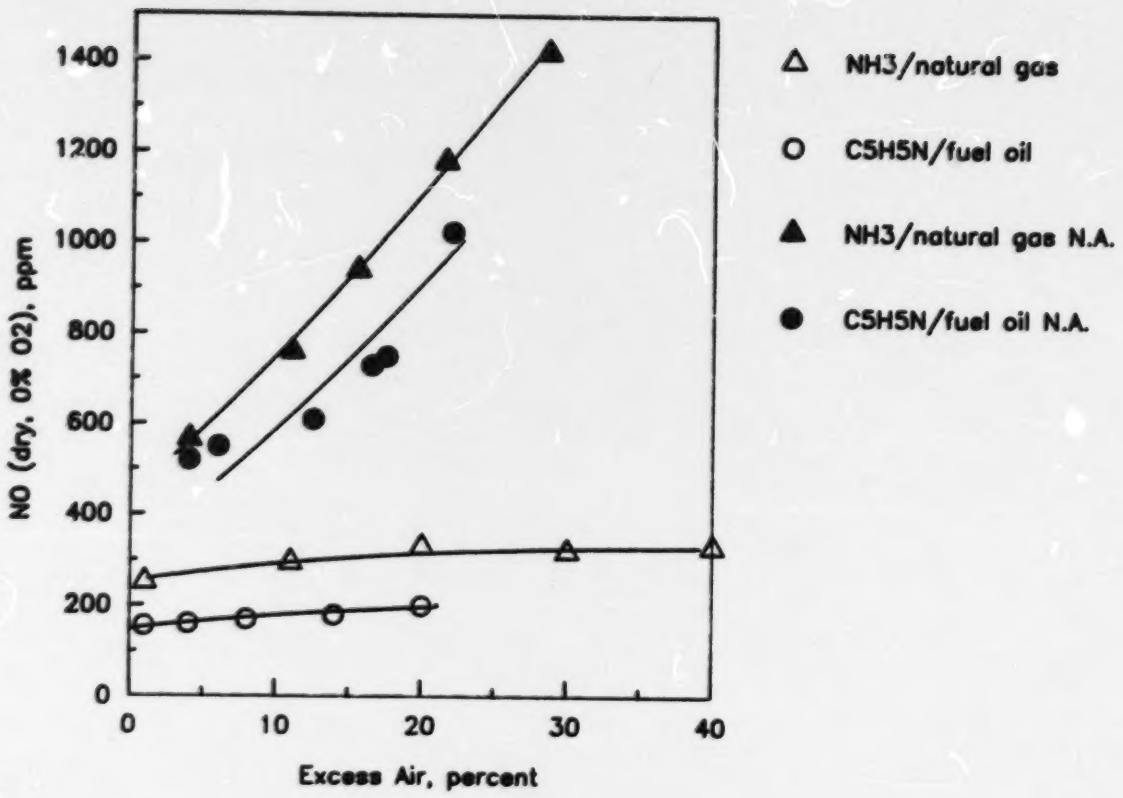

Figure 3. Effect of excess air on exhaust NO concentration from tests burning a 5.8 percent fuel nitrogen NH_3/natural gas and a 2 percent fuel nitrogen C_5H_5N/No. 2 distillate fuel oil mixtures. Curves with open symbols represent data from the low NO_x facility operated at optimum primary stoichiometries as shown in Figure 2. Curves with filled symbols represent corresponding data from the conventional North American (N.A.) boiler.

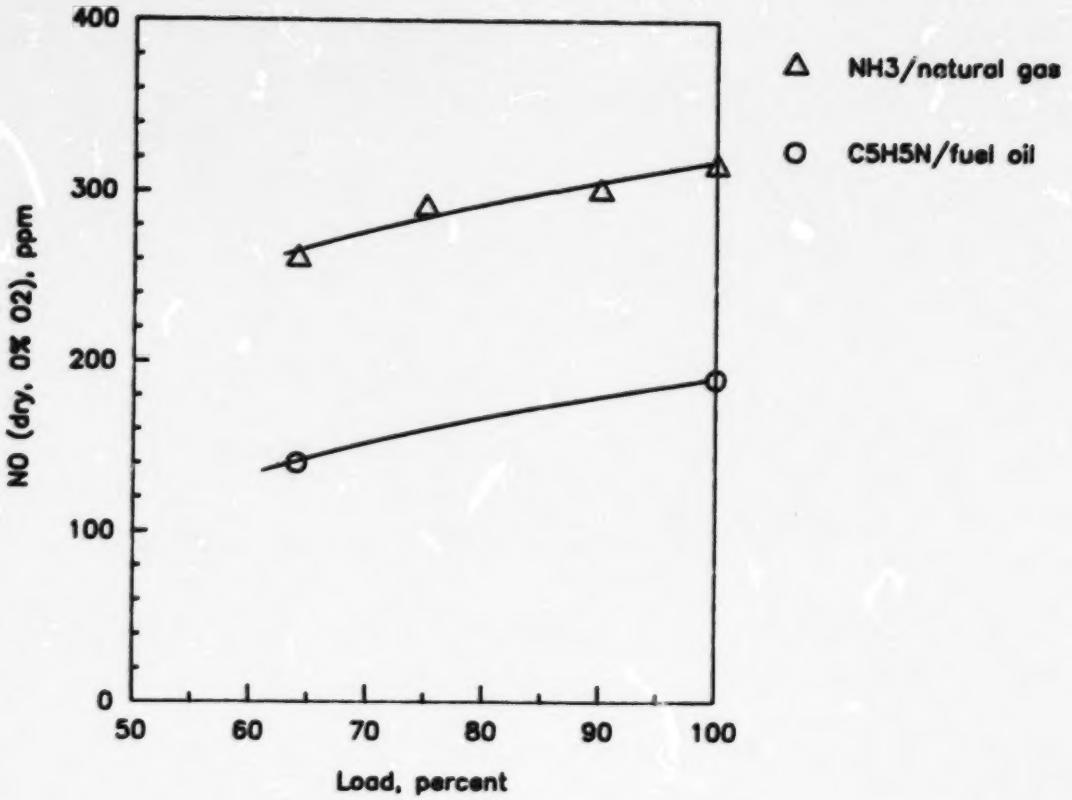

Figure 4. Effect of load variations on exhaust NO concentration from tests burning a 5.8 percent fuel nitrogen NH_3/natural gas and a 2 percent fuel nitrogen C_5H_5N/No. 2 distillate fuel oil mixtures (primary stoichiometries optimized).

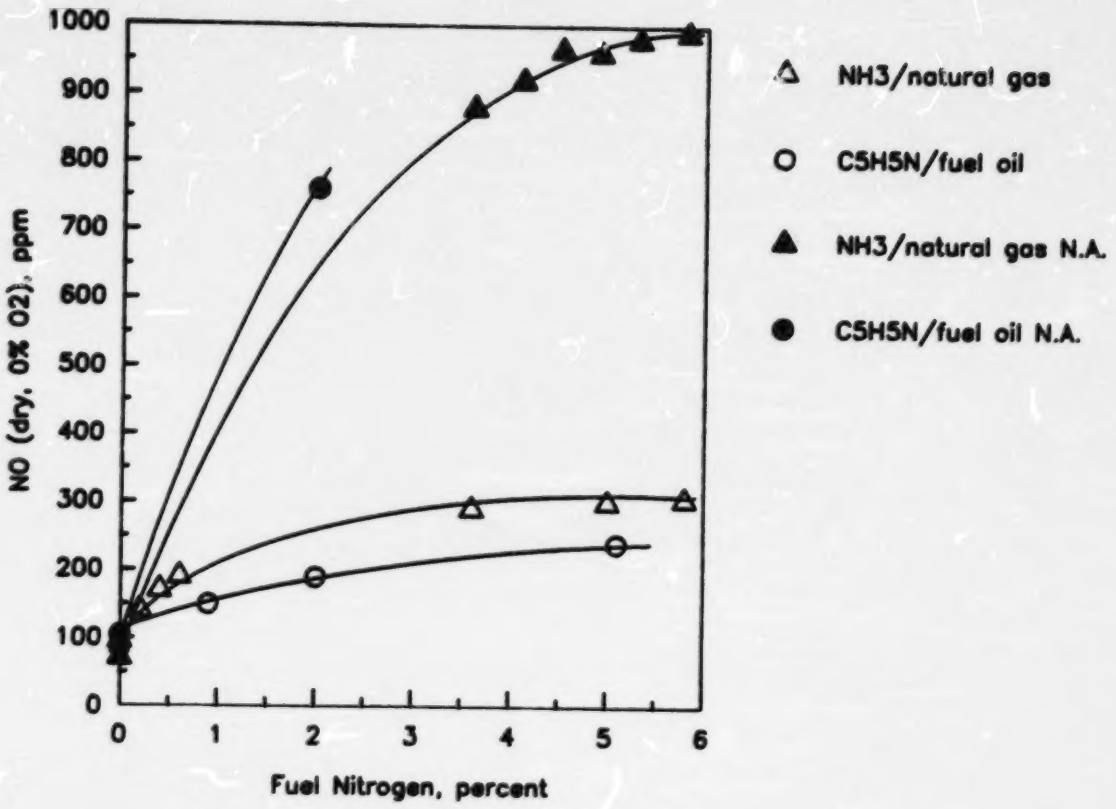

Figure 5. Effect of fuel nitrogen on exhaust NO concentration from tests burning NH_3/natural gas and C_5H_5N/No. 2 distillate fuel oil mixtures. Curves with open symbols represent data from the low NO_x facility (optimal primary stoichiometries). Curves with filled symbols represent corresponding data from the conventional North American (N.A.) boiler.

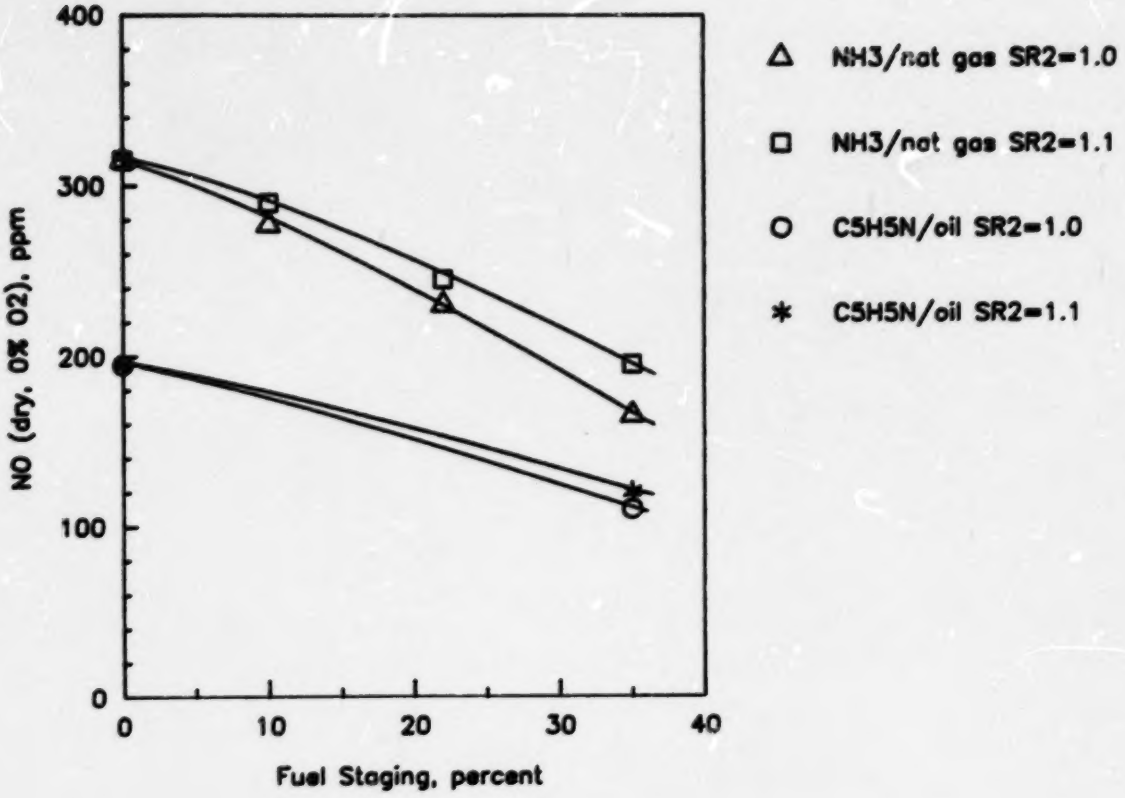

Figure 6. Effect of boiler fuel staging (reburning) on exhaust NO concentration from tests burning a 5.8 percent fuel nitrogen NH_3/natural gas and a 2 percent fuel nitrogen C_5H_5N/No. 2 distillate fuel oil mixtures. Natural gas data at two second stage stoichiometries (primary stoichiometry, SR1 = 0.78), and corresponding oil data at two second stage stoichiometries (primary stoichiometry, SR1 = 0.65) are presented.

TABLE 1

ANALYSIS OF DINOSEB PRODUCT USED FOR INCINERATION TESTS

Dinoseb in organic solvent (dinoseb product)

Analysis from Material Safety Sheet		Ultimate Analysis	
Dinoseb	54.4 %	C	65.01 %
Diesel #2	4.04 %	H	7.27 %
Xylene Range Aromatic	32.5 %	N	6.63 %
Inert	9.06 %	O*	20.45 %
		S	0.35 %
		Ash	0.29 %
		Moisture	0.63 %
		HHV	13,076 Btu/lb

---

*Oxygen by difference.

TABLE 2

EXPERIMENTAL TEST PLAN

Burner performance evaluation tests

Test	Condition	NO_x Control	Analyses
A	NH_3/natural gas 5.8% fuel nitrogen content	Vary first stage stoichiometry, excess air, load, fuel nitrogen content, reburning	CEM
B	C_5H_5N/No. 2 distillate fuel oil 2.0% fuel nitrogen content	Same as above.	SASS, CEM

Dinoseb recovery tests*

Test	Dinoseb Spike (ug)	Concentrate Volume (ml)	Analysis Concentration (ng/ul)
1A	100	10	10
1B	100	1	100
1C	1000	1	1000

Dinoseb product incineration tests

Test	Condition	NOx Control	Analyses
2	Combustion blank #2 fuel oil	Air staging	CEM, VOST, SASS
3	Combustion blank #2 fuel oil	Air staging and reburning	CEM, VOST, SASS
4	Dinoseb product scoping test (determine max dinoseb product conc. in No. 2 fuel oil for stable operation)	Air staging	CEM
5	100% dinoseb product	Air staging	CEM, VOST, SASS
6	100% dinoseb product	Air staging and reburning	CEM, VOST, SASS
7	100% dinoseb product	None	CEM

---

*For dinoseb recovery tests, standard dinoseb solutions (in dichloromethane) were spiked on 100 g XAD-2 resin, extracted, and concentrated.

TABLE 3

DINOSEB PRODUCT CEM AND PARTICULATE RESULTS*

Test	Condition	NO_x Control	SR1**	SR2	SR3	SR4	R/P %***
2	Combustion blank	Air staging	0.72	1.35	1.35	1.35	N/A
3	Combustion blank	Air staging and reburning	0.62	1.14	0.87	1.20	32.5
5	Dinoseb product	Air staging	0.64	1.23	1.23	1.23	N/A
6	Dinoseb product	Air staging and reburning	0.61	1.08	0.82	1.17	31.4
7	Dinoseb product	None	1.13	1.13	1.13	1.13	N/A

Test	NO (ppm)	NO_x (ppm)	CO (ppm)	CO_2 (%)#	THC (ppm)	Particulate (mg/dsm^3)	Temp1 (°C)##	Temp4 (°C)
2	78	-	9	-	-	4.13	-	-
	(52)		(6)			(2.75)		
3	89	-	13	-	-	5.02	-	-
	(59)		(9)			(3.35)		
5	141	128	6	-	2	151.34	1343	633
	(94)	(85)	(4)		(1)	(100.89)		
6	138	132	14	-	1	81.76	1151	652
	(92)	(88)	(9)		(0.7)	(54.51)		
7	4401	4497	13	-	1	-	708	606
	(2934)	(2998)	(9)		(0.7)			

---

*Stack emissions corrected to 0% oxygen. Emissions corrected to 7% oxygen are given in parentheses.
**SR1, SR2, SR3, SR4 indicate the stoichiometric ratios calculated at the combustor locations shown in Figure 1.
***R/P indicates gas reburning load/primary load (natural gas added in addition to primary burner load of 2,000,000 Btu/hr). (CEM concentrations have not been corrected for this dilution.)
#CO_2 concentrations are suspect and are not included due to instrument malfunction.
##Temp1, Temp4 indicate approximate gas temperatures (bare thermocouples, near the wall) measured at the combustor positions shown in Figure 1.

TABLE 4

DINOSEB PRODUCT POHC ANALYSES

Dinoseb recovery tests, instrument sensitivity 10 ng/ul

Test	Analysis Concentration (ng/ul)	Measured Concentration (ng/ul)	Percent Recovery
1A	10	ND*	N/A**
1B	100	ND	N/A
1C	1000	93.9	9.39

Incineration tests

Test	Condition	NO_x Control	Dinoseb Consumed (g)	Sample Vol as fraction of Stack Vol
2	Combustion blank	Air staging	0	0.00705
3	Combustion blank	Air staging and reburning	0	0.00276
5	Dinoseb product	Air staging	68130.7	0.00238
6	Dinoseb product	Air staging and reburning	76023.4	0.00275

Test	Potential Max. Dinoseb Conc. in Sample (g, ng/ul)	Dinoseb Conc. Measured in Sample (ng)	DRE Assuming 10 ng/ul Instrument Sensitivity, 100% Recovery	DRE Assuming 10 ng/ul Instrument Sensitivity, 9.39% Recovery
2	0	ND	N/A	N/A
3	0	ND	N/A	N/A
5	162.15, 4,054,000	ND	> 99.9998	> 99.997
6	209.31, 10,466,000	ND	> 99.9999	> 99.999

---

*Not detected.
**Not applicable.

TABLE 5

DINOSEB PRODUCT PIC ANALYSES

VOST samples (GC/MS)

Test	Condition	PICs Identified	ng	mg/sm^3	ppb
2A	Comb. blank w/ air staging	Benzene	2	< 0.001	< 1
3A	Comb. blank w/ air staging and reburning	Benzene	37	0.002	< 1
		SO_2	514	0.028	10.7
3B		Benzene	18	0.001	< 1
		SO_2	414	0.022	8.4
5A	Dinoseb product w/ air staging	Benzene	12	0.001	< 1
		Toluene	4	< 0.001	< 1
		Ethylbenzene	4	< 0.001	< 1
		Dodecane	22	0.001	< 1
		Naphthalene	1725	0.091	17.4
5B		Benzene	2	< 0.001	< 1
		SO_2	125	0.007	2.7
6	Dinoseb product w/ air staging and reburning	Benzene	9	0.001	< 1
		Toluene	10	0.001	< 1

SASS samples (GC/MS)

Test	Condition	PICs Identified	ng/ul	mg/sm^3	ppb
1A	Dinoseb spike	Unknown	25	N/A*	N/A
		Unknown	16	N/A	N/A
		Unknown	7	N/A	N/A
		Dichloro-iodo-benzene	12	N/A	N/A
2	Comb. blank w/ air staging	Unknown-phenyl	76	0.141	N/A
		Unknown	185	0.344	N/A
		Unknown	14	0.026	N/A
		Unknown-ester	6	0.011	N/A
		Dichloro-iodo-benzene	63	0.117	10.5
3	Comb. blank w/ air staging and reburning	Unknown-ester	43	0.160	N/A
		Dichloro-iodo-benzene	7	0.026	2.3
5	Dinoseb product w/ air staging	Unknown	13	0.141	N/A
		Unknown	10	0.109	N/A
		Styrene	8	0.087	20.5
		Dichloro-iodo-benzene	5	0.054	4.8
6	Dinoseb product w/ air staging and reburning	Unknown-ester	77	0.287	N/A
		Phthalate	21	0.078	N/A
		Dichloro-iodo-benzene	5	0.019	1.7

---

*Not applicable.